

ATTACHMENT H



**WATER
ANALYSIS
HANDBOOK**

Chlorine Dioxide

Method 8138

Direct Reading Method

HR (to 1000 mg/L)

Scope and Application: For water and wastewater



Tips and Techniques

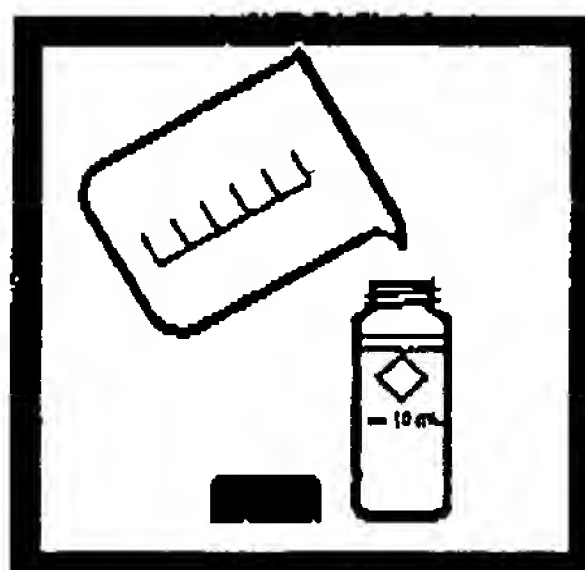
- Analyze samples immediately because chlorine dioxide is unstable and volatile. See *Interferences*.
- Wipe the outside of sample cells before each insertion into the instrument cell holder. Use a damp towel followed by a dry one to remove fingerprints or other marks.



Method 8138



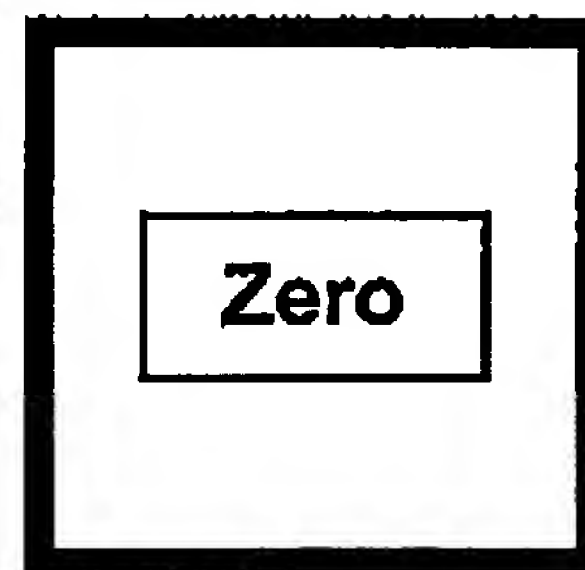
1. Touch
Hach Programs.
Select program
75 Chlor Diox HR.
Touch Start.



2. Fill a round sample cell to the 10-mL mark with deionized water. (This is the blank.)



3. Wipe the blank and place it into the cell holder.



4. Touch Zero.
The display will show:
0 mg/L ClO_2



5. Fill another sample cell to the 10-mL mark with sample. (This is the prepared sample.)



6. Wipe the prepared sample and place it into the cell holder.

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Chlorine Dioxide

Interferences

Interfering Substance	Interference Levels and Treatments
Acidity	Greater than 150 mg/L CaCO_3 . May not develop full color or color may fade instantly. Neutralize to pH 6–7 with 1 N Sodium Hydroxide (Cat. No. 1045-32). Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition (see Section 3.1.3 <i>Correcting for Volume Additions</i>).
Alkalinity	Greater than 250 mg/L CaCO_3 . Color may not develop fully or may fade instantly. Neutralize to pH 6–7 with 1 N Sulfuric Acid (Cat. No. 1270-32). Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for the volume addition (see Section 3.1.3 <i>Correcting for Volume Additions</i>).
Bromine, Br_2	Interferes at all levels.
Chlorine, Cl_2	May interfere at levels greater than 6 mg/L. Additional glycine may be able to compensate for this interference.
Chloramines, organic	May interfere.
Flocculating agents	High levels of most flocculating agents can be tolerated. This tolerance is decreased if chlorine is present. See the information about metals in this table. In the presence of 0.6 mg/L Cl_2 , $\text{Al}(\text{SO}_4)_3$ (< 500 mg/L) and FeCl_2 (< 200 mg/L) may be tolerated.
Hardness	No effect at less than 1,000 mg/L as CaCO_3 .
Iodine, I_2	Interferes at all levels.
Manganese, oxidized (Mn^{4+} , Mn^{7+}) or Chromium, oxidized (Cr^{6+})	Oxidized manganese interferes at all levels. Oxidized chromium interferes at levels greater than 2 mg/L. To remove the interferences: 1. Adjust sample pH to 6–7. 2. Add 3 drops Potassium Iodide (30 g/L) (Cat. No. 343-32) to a 25-mL sample. 3. Mix and wait one minute. 4. Add 3 drops Sodium Arsenite* (5 g/L) (Cat. No. 1047-32) and mix. 5. Analyze 10 mL of the treated sample as described in the procedure. Subtract the result of this test from the original analysis to obtain the correct chlorine dioxide concentration.
Metals	Various metals may interfere by combining with the glycine needed to remove the chlorine interference. Metal interference is limited except when chlorine is present. In the presence of 0.6 mg/L Cl_2 , both copper (>10 mg/L) and nickel (>50 mg/L) interfere. Other metals may also interfere, depending on their ability to prevent glycine from reacting with any Cl_2 in the sample. It may be necessary to add more glycine to overcome this interference.
Monochloramine	Causes a gradual drift to higher readings. When read within 1 minute after reagent addition, 3 mg/L monochloramine causes less than a 0.1 mg/L ClO_2 increase in the reading.
Ozone	Interferes at levels greater than 1.5 mg/L.
Peroxides	May interfere.
Extreme sample pH	Adjust to pH 6–7. See Section 3.3 <i>Interferences</i> on page 50.
Highly buffered samples	Adjust to pH 6–7. See Section 3.3 <i>Interferences</i> on page 50.

* Samples treated with sodium arsenite for interferences will be hazardous waste as regulated by Federal RCRA for arsenic (D004). See Section 5 for further information on proper disposal of these materials.

Sample Collection, Storage, and Preservation

Analyze samples for chlorine dioxide immediately after collection. Chlorine dioxide is a strong oxidizing agent and is unstable in natural waters. It reacts rapidly with various inorganic compounds, but oxidizes organic compounds more slowly. Many factors, including reactant concentrations, sunlight, pH, temperature, and salinity influence decomposition of chlorine dioxide in water.

BEST AVAILABLE COPY**Chlorine Dioxide**

Avoid plastic containers since these may have a large chlorine dioxide demand. Pretreat glass sample containers to remove any chlorine or chlorine dioxide demand by soaking in a dilute bleach solution (1 mL commercial bleach to 1 liter of deionized water) for at least one hour. Rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, only occasional pretreatment is necessary.

A common error in testing for chlorine dioxide is not obtaining a representative sample. If sampling from a tap, let the water flow for at least 5 minutes to ensure a representative sample. Let the container overflow with the sample several times, then cap the sample containers so there is no headspace (air) above the sample. If sampling with a sample cell, rinse the cell several times with the sample, then carefully fill to the 10-mL mark. Perform the chlorine dioxide analysis immediately.

Accuracy Check**Standard Solution Method**

Preparing chlorine dioxide standards is difficult and dangerous. In addition, these standards are both explosive and volatile! Only a trained chemist should prepare the standards using appropriate safety equipment and precautions. Hach does not recommend preparation of chlorine dioxide standards. If independent standard preparation is required, please see the instructions in *Standard Methods for the Examination of Water and Wastewater*, 20th ed., under the headings "Stock chlorine dioxide solution" and "Standard chlorine dioxide solution" (pp 4-74 and 4-75). Prepare a 500-mg/L chlorine dioxide standard.

Method Performance**Sensitivity**

Portion of Curve	Δ Abs	Δ Concentration
Entire range	0.010	5 mg/L ClO ₂

See Section 3.4.5 Sensitivity on page 54 for more information.

Summary of Method

Chlorine dioxide, a yellow gas, can be measured directly in a water solution. Test results are measured at 445 nm.

Required Reagents

Description	Quantity Required Per Test	Unit	Cat. No
Water, deionized	10 mL	4 liters	272-56

Required Apparatus

Sample Cells, 10-mL, w/cap	2	6/pkg	24276-06
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